Halomethanes in Tri-n-octylamine and Squalane Mixtures at Infinite Dilution

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The retention behavior of eight halomethanes and four saturated hydrocarbons was measured in gas chromatographic stationary phases consisting in tri-n-octylamine (TOA), squalane (SQ) and six TOA + SQ mixtures, at 55.0, 58.5, 62.5 and 65.0°C. Equlibrium constants for complex formation were extracted from experimental data by using a lattice model developed by Martire. The results may be interpreted in terms of the formation of weak hydrogen-bonded complexes, with sociation constants of about 0.13 L-mol^{-1} for haloforms and 0.07 L-mol^{-1} for dihalomethanes at 60°C.

KEY WORDS: Tri-*n*-octylamine; halomethanes; molecular association; hydrogen-bonded complexes; nonrandom mixtures; gas-liquid chromatography.

1. Introduction

Gas chromatography is a highly advantageous option to study molecular complexation equilibria. Systems to be studied must fulfil the requirement that one of the partners in the association (the additive) be a low vapor pressure liquid at the working temperature, while the other (the solute) is volatile enough as to be eluted from a gas chromatographic column. Two experimental approaches have been used: 1) the two-columns method of Martire and Rideal,[1] where association constants are calculated from retention data of complexing and alkane solutes from columns containing the additive and an inert solvent, both in the pure state, as the stationary phases; 2) in Purnell's[2]

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many-columns method complexing solutes are eluted from a series of columns whose stationary phases are solutions of the additive in an inert solvent. Several combinations of both approaches have also been used.[3,4]

Unfortunately no solvent is actually inert and, on the other side, solute-additive interactions different from that responsible for the formation of the complex are also feasible. Therefore, to obtain meaningful thermodynamic association constants it is necessary to discriminate between deviations from the ideal solution behavior attributable to the formation of the complex and those stemming from other origins, as combinatorial and free volume contributions and 'other end interactions.' With this purpose it is unavoidable to resort to some kind of molecular model.

The simplest model is the one that assumes that the complexing interaction is strong enough as to consider negligible all other types of nonidealities. This criterion, regularly applied in the early chromatographic complexation studies, is inappropriate for studying weak complexes. Ideally the model should be capable of dealing with interactions of different strength.

Several years ago the concept of degree of 'sociation' was introduced by Guggenheim[5] as the excess in the degree of association in a given mixture over that based on probabilities in a totally random mixture. Scott[6] went further into this matter utilizing a lattice of monomeric donor, acceptor and inert solvent molecules; non-randomness was introduced by means of quasi-chemical calculations, considering that all interaction energies are equal except that between a given pair of 'faces'.

Scott's model was extended by Martire[7] to cover mixtures of heterogeneous molecules of different sizes: solute (a), inert solvent (b) and additive (c) molecules contain r_a, r_b and r_c segments, respectively; solute molecules are constituted by type 1 and type 2 segments, with fractions f_{1a} and f_{2a}, respectively; inert solvent molecules are chemically homogeneous, with all of their segments being of type 3 (paraffinic); additive molecules have a fraction f_{3c} of segments of type 3 and a fraction f_{4c} of type-4 segments. The formation of an i-j pair and a 3-3 pair from i-3 and j-3 pairs is characterized by the exchange energy $\Delta W_{ij} = (w_{ij} + w_{33}) - (w_{i3} + w_{j3})$. This definition makes $\Delta W_{13} = \Delta W_{23} = \Delta W_{34} = 0$; however, as a first order approximation it is assumed that $|\Delta W_{ij}| \ll kT$ for all the segment pairs except for the 2-4 pair. Martire applied this assumption together with quasi-chemical and conservation equations to correct the results for the different pair numbers deduced for random

pairing and to obtain an expression for the partial molar excess configurational energy of the solute at infinite dilution. If it is further assumed that the free volume contributions are negligible (which shall be the case when additive and inert solvent thermal expansion coefficients are close enough) it can be shown that the solute infinite dilution vapor-liquid partition coefficient in a mixed solvent $K^o_{a(m)}$ is related to that in the pure inert solvent $K^o_{a(b)}$ by

$$\ln\,[K^o_{a(m)}/K^o_{a(b)}] = r_a(r_c^{-1} - r_b^{-1})\phi_c - zr_af_{1a}(\phi_cf_{4c})(\Delta W_{14}/kT)$$

$$+ zr_af_{2a}\ln\,[1 + K^o_{ac}\phi_c/V^o_c] - zr_a(\phi_cf_{4c})^2(\Delta w_{34}/kT) \qquad (1)$$

where z is the lattice coordination number, V^o_c and ϕ_c represent the additive molar volume and volume fraction in the mixture, r_i is the ratio between the solute and a reference solute (methylene chloride in the present paper) molar volume, $\Delta w_{34} = w_{34} - (1/2)(w_{33} + w_{44})$ is the usual interchange energy, and K^o_{ac} is the thermodynamic solute-additive excess or sociation constant, related to the corresponding association constant K_{ac} by

$$K^o_{ac} = K_{ac} - K^r_{ac} = f_{4c}V^o_c(\kappa - 1) \qquad (2)$$

In this equation K^r_{ac} random pairing and $\kappa = \exp(-\Delta W_{24}/kT)$.

Expressions pertinent to some particular cases of importance for the application of the model are deduced from Eq. (1). In the random mixing limit ($\kappa \rightarrow 1$), for instance

$$\ln[K^o_{a(m)}/K^o_{a(b)}] = r_a(r_c^{-1} - r_b^{-1})\phi_c - zr_af_{1a}(\phi_cf_{4c})(\Delta W_{14}/kT)$$

$$- zr_af_{2a}(\phi_cf_{4c})(\Delta W_{24}/kT) - zr_a(\phi_cf_{4c})^2(\Delta w_{34}/kT) \qquad (3)$$

and the equation for a chemically homogeneous solute is obtained by making $f_{1a} = 0$ in Eq (3). For a paraffin (p) solute,

$$\ln[K^o_{p(m)}/K^o_{p(b)}] = r_p(r_c^{-1} - r_b^{-1})\phi_c - zr_a(\phi_cf_{4c})^2(\Delta w_{34}/kT) \qquad (4)$$

Substracting Eq. (4) from Eq. (1):

$$Q + \varepsilon = -zr_af_{1a}(\phi_cf_{4c})(\Delta W_{14}/kT) + zr_af_{2a}\ln\,[1 + K^o_{ac}\phi_c/V^o_c] \qquad (5)$$

where

$$Q \equiv \ln[K^{o}_{a(m)}K^{o}_{p(b)}/K^{o}_{a(b)}K^{o}_{p(m)}] \tag{6}$$

and

$$\varepsilon \equiv (r_p - r_a)[(r_c^{-1} - r_b^{-1})\phi_c - z(\Delta w_{34}/kT)(f_{4c}\phi_c)^2] \tag{7}$$

An important aspect of these equations is that only relative retention times need to be measured to calculate Q. ε is a correction term that takes into consideration molecular size differences between solutes a and p. When the measurements have been made at several temperatures Eq. (2) and the definition of κ can be introduced into Eq. (6) to give

$$Q + \varepsilon = A(\phi_c/T) + \ln\{1 + [exp(C/T) - 1]\phi_c f_{4c}\} \tag{8}$$

where $A = -zr_a f_{1a} f_{4c}(\Delta W_{14}/k)$ and $C = -\Delta W_{24}/k$; the assignment $zr_a f_{2a} = 1$ has been made, implying that only one of the zr_a solute molecule sites participates in the strong interaction (which is fully justified for hydrogen-bonding). A nonlinear least-squares fit of Eq. (8) to the experimental data yields the parameters A and C; from C not only the values of K^{o}_{ac} at several temperatures can be obtained, but also ΔH^{o}_{ac} and ΔS^{o}_{ac}, the standard enthalpy and entropy of excess complex formation. Similarly, from Eq. (3) and Eq. (4), we have for the random mixing limit

$$Q + \varepsilon = D(\phi_c/T) \tag{9}$$

with

$$D = -zr_a f_{4c}(f_{1a}\Delta W_{14} + f_{2a}\Delta W_{24})/k \tag{10}$$

Results for the systems halomethane (HM) + di-n-octyl ether (DOE) + n-octadecane[9] and HM + tri-n-octylphosphine oxide (TOPO) + squalane (SQ)[10,11] were analyzed by means of this model. HM + TOPO complexes are highly stable ($K^{o}_{ac} = 8.92$ L-mol^{-1} for chloroform at 60 °), the plots of $Q + \varepsilon$ vs ϕ_c display a pronounced curvature and no linear contribution is necessary in the fit of Eq. (8) to experimental data, which may be imputed to large differences between the strengths of the 2-4 (X_3C-H...OPR, X halogen) and 1-4 (HX_2C-X...OPR) interactions that make the consideration of this last type of interaction unnecessary. Much less strong complexes are formed between HM and DOE ($K^{o}_{a(m)} = 0.308$ L-mol^{-1} for chloroform at 30°C), and the contribution of the lineal term in Eq. (8) is not negligible.

In the present paper the results obtained for eight HM plus

tri-n-octylamine (TOA) at 55.0, 58.5, 62.5 and 65.0°C, using four saturated hydrocarbons as reference solutes, are reported. Earlier studies[12-14] indicate that when alkyl chains are of approximately equal sizes, tri-n-alkylamines + HM complexes are weaker than those formed between HM and di-n-alkylethers. TOA was expected to be a weak HM complexing agent, a good example to study both the lower limits of the method and the possibility of distinguishing between two types of interaction under these circumstances. Squalane was chosen as the inert solvent because its thermal expansion coefficient (8.15×10^{-4} K^{-1} at 20°C)[15] is almost identical with that of TOA (8.32×10^{-4} K^{-1} at 25°C)[16]; on the other side, since SQ a branched paraffin, short range orientational order should be absent from its mixtures.

2. Experimental

The glc apparatus consisted of a Perkin-Elmer Sigma 300 gas chromatograph, equipped with a thermal conductivity detector and an LCI-100 computing integrator, with modifications that were described in an earlier publication;[17] a Haake N3B water bath was used as column thermostat. Hydrogen, previously passed through a trap containing molecular sieve 5A, was used as the carrier gas. Columns were made from 0.53 cm i.d. stainless steel tubes, 0.6-1.0 m in length.

TOA (Aldrich Chemical Co.) was purified by distillation under reduced pressure; SQ (Hewlett-Packard) was used as received. Chromosorb W (AW DMCS treated 60/80 mesh) was used as the solid support; packings contained between 6 and 8% by weight of stationary phase. Retention data were obtained for pure SQ and the following weight fractions of TOA: 0.192, 0.335, 0.488, 0.695, 0.762, 0.891 and 1.000. Densities at five temperatures within the range 50-65°C were measured for TOA, SQ and three mixtures using a 5 mL pycnometer. Since excess volumes were less than 0.1%, volume fractions were computed from weight fractions and pure component densities at each temperature.

All the solutes were more than 99 moles per cent pure, and were used without further purification. n-Hexane, n-heptane, n-octane and cyclohexane were used as reference solutes. Solute vapors, together with one or two of the reference hydrocarbons and a small quantity of methane were injected by means of 100 and 250 µL Hamilton syringes. Relative retentions were computed from the HM and reference hydrocarbon peak maximum retention times in the same chromatogram after dead volume corrections using the methane peak.

3. Results and Discussion

There are several options to calculate the correction term ε. Martire[9] used a method based on the measurement of the retention time for a solute with the same functional group as the additive solvent; it could not be applied in the present work because amines tail severely in most chromatographic columns, thus precluding the collection of thermodynamically meaningful retention data. For that purpose we applied the equation

$$\ln[K^0_{P(m)}K^0_{P'(b)}/K^0_{P(b)}K^0_{P'(m)}] = (r_p - r_{p'})(r_c^{-1} - r_b^{-1})\phi_c)$$

$$- \Phi(r_p - r_{p'})\phi_c^2 \qquad (11)$$

where $\Phi = zf_{4c}^2(\Delta w_{34}/kT)$ obtained by substracting from Eq. (4) the equation corresponding to a second hydrocarbon solute p'. Equation (11) involves only relative retentions, and the value of Φ can be calculated from the slope of the straight line obtained by plotting the lefthandside against ϕ_c^2. Choosing cyclohexane as the reference solute, the mean of the values of Φ obtained with the remaining hydrocarbons was 0.013 ± 0.001 at 55C; this result was introduced into Eq. (7) to calculate the values of ε. Solute molar volumes necessary for these and following calculations were obtained from the literature.[18,19]

In Fig. 1 can be found a plot of $Q + \varepsilon$ vs. ϕ_c/T for bromotrichloromethane. A linear least-squares treatment indicates: slope 41.2 ± 0.77 K ($\pm$ indicates the standard deviation), intercept 0.002 ± 0.0015, correlation coefficient 0.998; the same treatment for carbon tetrachloride data results in: slope 20.0 ± 0.61 K, intercept -0.002 ± 0.0012, and correlation coefficient 0.993. The intercepts are quite small and of little statistical significance. With zero intercept assumed the slopes are 42.1 ± 0.37 K for bromotrichloromethane and 18.8 ± 0.31 K in the case of carbon tetrachloride. Data for both solutes seem to be satisfactorily accounted for by Eq. (9) (i.e., by the random pairing assumption).

The value of $\Delta W_{14}/k$ for the Cl-N interaction can be deduced from the slope of the carbon tetrachloride plot: $D = -zr_a f_{4c}(\Delta W_{14}/k)$. To this end $f_{4c} = 0.0166$ is estimated from Bondi's[20] compilation of van der Waals volumes; then the assignment $zr_a f_a = 1$ with $f_{2a} = 0.0945$ is made for chloroform, from which $zr_a = 13.1$ is deduced for carbon tetrachloride on the assumption that the total number of contacts is directly proportional to the molecular size. On these bases, $\Delta W_{14}/k = -87$ K, a result considerably smaller than $\Delta W_{14}/k = -230$ K obtained by Martire and collaborators for the system CCl_4 + DOE. Charge transfer
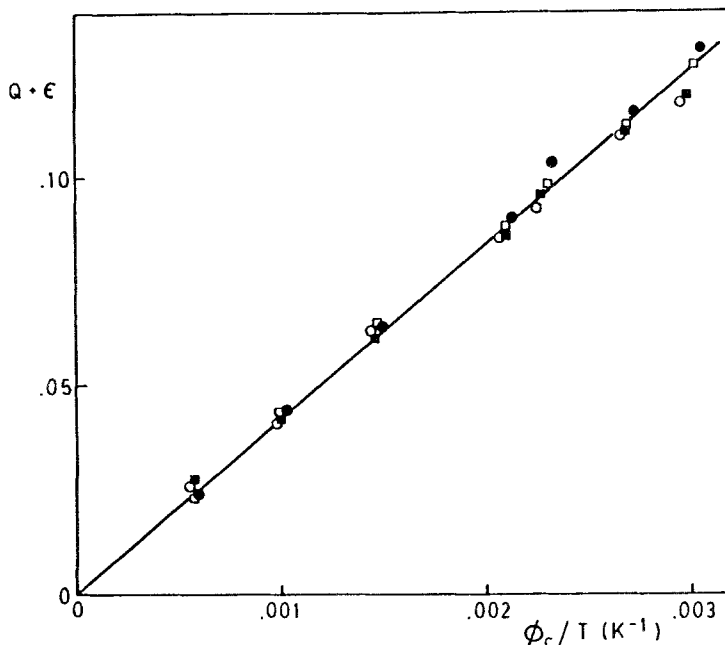
Fig. 1. Plot of $Q + \varepsilon$ *vs.* ϕ_c/T for the solute bromotrichloromethane:
●, 55°C; □, 58.5°C; ▫, 62.5°C; O, 65°C.

$(n \rightarrow \sigma^*$ type) between an n-donor and an acceptor halogen atom, and dipole-induced dipole , are the most probable mechanisms of interaction for these systems.[12,13,21,22] The stronger interaction manifested by DOE could be explained on the basis of steric considerations, its O atom being more accessible than the N atom in TOA. Bromotrichloromethane, a permanent dipole, constitutes a particular case that shall be discussed later.

Shown in Fig. 2 is a plot of $Q + \varepsilon$ *vs.* ϕ_c for chloroform at 55°C. The plots for the three haloforms studied are very much alike, their curvatures being markedly smaller than those shown by the plots obtained for the same solutes in TOPO or DOE; the plots for the dihalomethane solutes display the smallest curvatures. Nonlinear fits of $Q + \varepsilon = f(\phi_c, T)$ were performed by using the Marquardt-Levenberg[23] algorithm.[4] Attemps to fit Eq. (8) to experimental data resulted in small A parameters with large standard deviations but C parameters were calculated with

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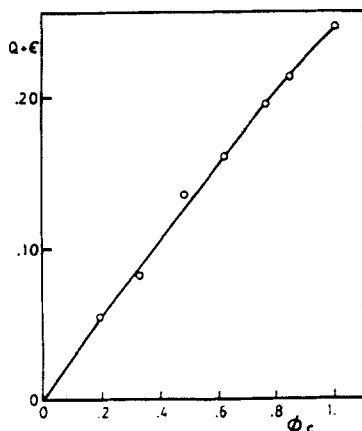[4]Used in the SigmaPlot 4.1 program (Jandel Scientific, San Rafael, CA.

Fig. 2. Plot of $Q + \varepsilon$ vs. ϕ_c at 58.5°C for the solute chloroform.

better precision. Parameter dependencies,[5] however, were greater than 0.998 suggesting that the model was overparameterized and that a model with fewer parameters would be better. Overparameterization can mean that the model is inappropriate or the data are not adequate for estimating all the parameters. In our opinion there are neither inadequacies in the model nor low quality in the data; the fact is that the systems we are dealing with are characterized by small A parameters, as indicated by the very weak Cl-N interactions detected during the work with carbon tetrachloride. Difficulties in separating both contributions to $Q + \varepsilon$ were encountered by Martire et al.[9] during their work with haloform + DOE systems, in spite of stronger other end interactions.

On the basis of these findings, experimental data were fitted to Eq. (8) assuming $A = 0$. The results are listed in Table I, where the values of K_{ac}^o at 60.0°C are also included. The haloforms sociation constants reveal weak hydrogen-bonded complexes and, as could have been foreseen, dihalomethane complexes are still weaker. Although the K_{ac}^o for the three haloforms are roughly the same within the error limits, it seems feasible to expect a trend towards increased complex stability as Cl atoms are substituted for Br atoms in the solute molecule. No such trend is detected with the dihalomethanes. From Eq. (2), the expression for the standard enthalpy of excess complex formation is obtained.

$$\Delta H_{ac}^o = R\{\alpha T^2 - C/[1 - \exp(-C/T)]\} \qquad (12)$$

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[5]Parameter dependence = 1 − (parameter variance other parameters held constant / parameter variance allowing other parameters to change in the usual way).

Table I. Results of Analysis of Chromatographic Data
According to Eqs. (2,8,12) at 60°C

Solute	C	K_{ac}^{o}	$-\Delta H_{ac}^{o}$
$CHCl_3$	946 ± 30	0.121 ± 0.012	7.52 ± 0.22
$CHCl_2Br$	974 ± 50	0.132 ± 0.021	7.72 ± 0.37
$CHClBr_2$	992 ± 32	0.140 ± 0.014	7.85 ± 0.24
CH_2Cl_2	757 ± 29	0.065 ± 0.006	6.18 ± 0.20
CH_2ClBr	777 ± 40	0.070 ± 0.009	6.32 ± 0.28
CH_2Br_2	755 ± 55	0.065 ± 0.012	6.17 ± 0.36

[a] Units: C, K^{-1}; K_{ac}^{o}, L-mol^{-1}; ΔH_{ac}^{o}, kJ-mol^{-1}..

where α is the additive thermal expansion coefficient (9.0×10^{-4} K^{-1} at 60°C). Results obtained at 60°C can also be found in Table I. Since K_{ac}^{o} and ΔH_{ac}^{o} are calculated from C, there is an obvious correlation between both sets of thermodynamic properties.

Bromotrichloromethane represents an intermediate case between carbon tetrachloride and the haloforms and the dihalomethanes. $\Delta W_{24}/k$ can in principle be calculated from its relatively large D parameter by introducing into Eq. (10) zr_a, f_{4c}, f_{1a} and f_{2a} estimations from van der Waals volumes[20] and by assuming that $\Delta W_{14}/k$ retains the same value as in carbon tetrachloride (an assumption of dubious validity in the presence of a permanent dipole moment). Such a calculation leads to $\Delta W_{24}/k = -460$ K, a result that by no means guarantees random mixing for CCl_3Br + TOA mixtures but which can be used in Eq. (2) to obtain $K_{ac}^{o} = 0.02$ L-mol^{-1}. This value is not large enough to give rise to curved $Q + \varepsilon$ vs ϕ_c plots, but it is debatable whether the interaction represents a collision interchange or if a labile complex is formed. Bromotrichloromethane is probably a border case where Martire's model is unable to give a definite answer.

Acknowledgment

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